

**Characterization and Development of Advanced Materials:
Role & Understanding of Interfacial Phenomena (Congressional)**

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FINAL REPORT

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By

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Preface

The scientific activities carried out in this project focused on characterization and development of advanced materials. These activities were divided into three parts. Part I focused on nanophase enhanced optical devices: development of transparent ceramics for infrared window and laser applications, and development of nanocomposites for photovoltaic applications. . Part II focused on alternative energy storage using first-principles modeling and simulations. The research in Parts I and II was carried out at Washington State University. Part III focused on charge transport in solid oxide fuel cells (SOFC) and organic light emitting diodes (OLED). The research in Part III was carried out, under a subcontract, at the Pacific Northwest National Laboratory (PNNL).

Because of the distinct nature of the three projects in this grant, the text of this final report consists of the activities for each of these three projects.

Dr. Judah Goldwasser, the ONR Program Manager for this project, is sincerely thanked for his strong interest in the work.

Part I

Nanophase Enhanced Optical Devices

Hergen Eilers, Principal Investigator
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Abstract

The overall work focused on Nanophase Enhanced Optical Devices. Two projects *Transparent Ceramics for Infrared Window and Laser Applications*, and *Broadband-Absorbing Polymer-Metal Nanocomposites for Photovoltaic Applications* comprised this effort. The objectives for the first project were (i) to fabricate transparent yttria ceramics from commercially available nanopowder with a grain size significantly smaller than 100 μm and a transmittance in the infrared close to the theoretical maximum; and (ii) to fabricate polycrystalline Er,Yb:Y₂O₃ ceramics, suitable as solid-state laser materials in the eye-safe wavelength range. The objective for the second project was to fabricate an organic photovoltaic device that absorbs solar radiation between 400 nm and 2500 nm and has a power conversion efficiency of 5% or better. A research laboratory was set up to synthesize, process, and characterize ceramic materials and polymer-metal nanocomposites. A transparent yttria ceramic with an average grain size of about 20 μm and good optical transparency was prepared and characterized. Yttria nanoparticles codoped with erbium and ytterbium were successfully prepared and characterized. Polymer-metal nanocomposites were successfully prepared and it was demonstrated that their absorption spectrum can be tailored to match the solar radiation.

Background/Problem Statement

1. Transparent Ceramics for Infrared Window and Laser Applications

a. Infrared Window Applications

"Heat-seeking" missiles such as the Sidewinder missile rely on a transparent dome at the tip of the missile to transmit optical signals to the sensor and to protect the sensor from harsh environmental conditions. These domes need to be mechanically strong to protect the sensor from rain, sand, and insect damage during flight. At the same time their optical properties must be such that they transmit all required optical signals with minimal interference.

Interference to the optical signal can arise from various causes. Some domes are made from birefringent materials such as sapphire, leading to double images on the sensor. Another source of optical interference is the emissivity of the dome material at high temperatures. As a missile travels at speeds of Mach 3 and above, the tip can heat up to several hundred degrees Celsius. At these temperatures the dome material itself starts to emit radiation, causing a background noise signal that can potentially overshadow the target signal.

Unfortunately, no one material meets all the requirements optimally, so trade-offs have to be made between mechanical and optical performance.¹ While sapphire has the best mechanical properties, yttria

¹ D. C. Harris, *Materials for Infrared Windows and Domes* (SPIE Press, Bellingham, WA, 1999).

has superior optical properties. In particular, its emissivity is significantly lower than that of the other materials. However, its mechanical strength and therefore its resistance to thermal shock are not as good as those of other materials and thus yttria is not used for applications that involve rapid heating.

However, it is possible to improve the mechanical properties of polycrystalline materials such as yttria. The mechanical strength of a material is a function of the grain size. As the grain size decreases the mechanical strength increases. Moreover, the resistance to thermal shock is directly proportional to the mechanical strength. Thus, the resistance to thermal shock also increases with smaller grain size.

Current yttria ceramics have a grain size of several hundred micrometers. Doping with La_2O_3 has been successfully used to reduce the grain size by about a factor of 2. However, the addition of La_2O_3 to yttria significantly reduces the thermal conductivity k and therefore the resistance to thermal shock of this material. Thus, dopants such as La_2O_3 are to be avoided and alternative means to decrease the grain size need to be developed.

b. Laser Applications

High-power lasers, operating at "eye-safe" wavelength, are of interest for military applications because they can quickly deliver energy over long distances, and, unlike conventional weapons, they have a deep magazine. The best solid-state laser to date operates at about 25-30 kW. This laser, the solid-state heat-capacity laser (SSHCL), is currently being developed at Lawrence Livermore National Laboratory (LLNL).² In the SSHCL system, about 50% of the pump energy from the diode lasers is converted into light output; the remaining 50% is converted into high-intensity heat. Unless this heat is removed from the solid-state laser material (gain media), the laser will stop functioning or suffer irreparable damage. The SSHCL operates for about 10 to 20 seconds before it is shut down for a period of 30 seconds to several minutes while the gain media is cooled by two cold copper plates. After the cooling cycle, the laser is turned back on for another 10 seconds. While this operating process significantly reduces thermal stress during lasing operation, the gain media experiences a thermal shock each time the cold copper plates are applied to the hot surface of the gain media.

The prototype SSHCL used neodymium-doped glass (Nd:glass) as the gain media. The current version of the laser uses neodymium-doped gadolinium gallium garnet (Nd:GGG), which has much better thermal properties than Nd:glass. This is very important for the SSHCL, in which the gain media is subjected to rapid changes in temperature, resulting in thermal shock. The resistance to thermal shock is mainly a function of the thermal conductivity and thermal expansion of the material.³ The higher the thermal conductivity and the smaller the thermal expansion, the better the resistance to thermal shock.

While Nd:GGG has much better properties than Nd:glass, there are limits to how big these crystals can be grown while maintaining sufficient quality. Sesquioxides such as yttria (Y_2O_3) have even better thermal properties than garnets such as GGG, but sesquioxides have very high melting temperatures and experience high-temperature phase changes, making it very difficult to grow single crystals. However, these materials can be fabricated in polycrystalline (ceramic) form, by sintering the sesquioxide powder. The powder particles need to be sufficiently small to avoid optical scattering on the grains and grain-boundaries. A fully-dense transparent neodymium-doped Y_2O_3 ceramic laser material with grain sizes significantly smaller than the wavelength of the laser light is expected to have a resistance to thermal shock at least twice as high as that of Nd:GGG.^{4, 5, 6}

² A. Parker, "Bright Future for Compact Tactical Laser Weapons," *LLNL Science & Technology Review*, April 2002, 19; and A. Parker, "World's Most Powerful Solid-State Laser," *LLNL Science & Technology Review*, October 2002.

³ R. Gaume and B. Viana, "Optical and Thermo-Mechanical Properties of Solid-State Laser Materials," *Ann. Chim. Sci. Mat.* 28, 89 (2003).

⁴ A. A. Kaminskii, *Laser Crystals*, 2nd Ed., Springer Series in Optical Sciences, Springer-Verlag Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong (1990).

⁵ http://www.mt-berlin.com/frames_cryst/descriptions/substrates.htm

An even more fundamental problem for the development of high-energy / high-power lasers is the need to scale-up the size of the gain media to achieve the required gain. The size of single crystals is limited by the growth technique. The growth process can take up to several months and requires large amounts of electrical power. The above mentioned Nd:GGG can currently be grown in sizes of up to 12 cm in diameter. To achieve their goal, the designers will have to increase the size of the gain media to 15 cm in diameter.

The only limit to the size a laser ceramic can be fabricated is the size of the furnace. Ceramic laser materials also have other potential advantages. The dopant concentration of the starting material can be adjusted so that thermal gradients over the gain media are minimized. In addition, different activator ions could be mixed and consolidated into the same ceramic, allowing the use of multiple laser wavelengths within the host material. This effect would also allow the integration of materials with different optical functions, such as gain media and Q-switch, into one larger device. Lastly, more complex cooling channels could be integrated into the material.

2. Broadband-Absorbing Polymer-Metal Nanocomposites for Photovoltaic Applications

As global oil supply issues become more and more challenging, energy generation, conversion,⁶ and storage is becoming of broad interest to the U.S. and its military branches. With the Navy transforming its fleet to the "all-electric ship," ONR's Ship Systems and Engineering Research Division is actively pursuing research in the area of energy generation, conversion, and storage. Photovoltaic devices with significantly enhanced conversion efficiencies and reduced cost/watt are of interest to replace or complement other energy sources for applications from integrated electronic circuits to large arrays mounted on ships, aircrafts and satellites.

The main technical limitation to all photovoltaic systems is the limited wavelengths sensitivity of the materials being used, resulting in low efficiencies. Inorganic semiconductor devices often consist of stacked materials with different wavelengths responses. However, this approach adds significant cost to the device. Dyes are often used in organic and photochemical photovoltaic devices to sensitize the materials and increase the wavelengths range. However, to cover the complete solar spectrum, multiple dyes would have to be used. Availability of dyes, unwanted interferences of the different dyes, and costs limit this approach.

A potential solution to the limited absorption range is the use of nanostructured metals, which have been shown to absorb light over a broad range of wavelengths. In an effort to increase the sensitivity of photovoltaic devices, nanostructured metals are embedded into polymer/organic solar cell materials.

In this design, nanostructured metals such as silver (Ag) are embedded in a polymer/ organic matrix consisting of a polymer such as PMMA, Teflon AF, etc., an electron acceptor such as [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM), C₆₀, or tris (8-quinolinolato) aluminum (Alq₃), and a hole-transporting material such as poly(3-hexylthiophene) (P3HT), poly-2-methoxy-5-(2'-ethyl-hexoxy)-1,4 para-phenylene-vinylene (MEHPPV), or N,N'-bis-(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (NPB). The functionality is based upon the absorption of solar radiation by the metallic nanoparticles through the excitation of surface plasmons. Subsequently, electrons are transferred to the electron acceptor which conducts the electrons to one of the electrodes. Holes are transported via the hole-transporting material to the counter electrode.

⁶ J. J. Derby and Q. Xiao, "Some effects of crystal rotation on large-scale Czochralski oxide growth: analysis via hydrodynamic thermal-capillary model," *J. Cryst. Growth* 113, 575 (1991)

Objectives

1. Transparent Ceramics for Infrared Window and Laser Applications

a. Infrared Window Applications

The overall project objective was to fabricate a transparent yttria ceramic using commercially available nanopowder. The grain size of the ceramic was supposed to be significantly smaller than 100 μm and the transmittance in the infrared was supposed to be close to the theoretical maximum.

b. Laser Applications

The overall project objective was to fabricate polycrystalline Er,Yb:Y₂O₃ ceramics, suitable as solid-state laser materials in the eye-safe wavelength range.

2. Broadband-Absorbing Polymer-Metal Nanocomposites for Photovoltaic Applications

The overall project objective is to fabricate an organic photovoltaic device that absorbs solar radiation between 400 nm and 2500 nm and has a power conversion efficiency of 5% or better.

Technical Approach by Task

1. Transparent Ceramics for Infrared Window and Laser Applications

a. Infrared Window Applications

To accomplish the objective, published data regarding the powder processing and sintering of yttria were used as a starting point. Design of experiments (DOE) was used to determine the most suitable processing parameters. The following tasks were deemed necessary to achieve the objective of the project: (i) Characterize morphology of commercially available yttria nanopowder, (ii) Develop processing steps for green body formation, (iii) Develop sintering process, (iv) Develop hot-isostatic pressing (HIP) process, (v) Develop lapping and polishing process, (vi) Characterize optical transmittance and morphology of ceramics, (vii) Measure hardness of ceramics, and (viii) Provide samples for further testing to D. C. Harris (Chemistry and Materials Division, Naval Air Warfare Center, China Lake, CA).

b. Laser Applications

To accomplish the objective, the first task was to develop a synthesis process for Er,Yb:Y₂O₃ nanoparticles. Next, the suitability of the Er,Yb:Y₂O₃ nanoparticles was evaluated by characterizing the morphological and optical properties. The subsequent tasks are: (i) Develop processing steps for green body formation; (ii) Develop sintering process; (iii) Develop hot-isostatic pressing (HIP) process; (iv) Develop lapping and polishing process; (v) Characterize optical and morphological properties of Er,Yb:Y₂O₃ ceramics; and (vi) Test laser properties of Er,Yb:Y₂O₃ ceramics.

2. Broadband-Absorbing Polymer-Metal Nanocomposites for Photovoltaic Applications

To accomplish the objective, published data regarding the synthesis of polymer-metal nanocomposites was used as a starting point. The following tasks were deemed necessary to achieve the objective of the project: (i) Develop deposition process for metals, polymers, organics, and composites; (ii) Prepare polymer-metal nanocomposites; (iii) Characterize morphological and optical properties of polymer-metal nanocomposites; (iv) Characterize

electrical properties of polymer-metal nanocomposites; (v) Prepare polymer – metal – hole-transporting – electron-acceptor nanocomposites; (vi) Characterize morphological and optical properties of polymer – metal – hole-transporting – electron-acceptor nanocomposites; (vii) Characterize electrical properties of polymer – metal – hole-transporting – electron-acceptor nanocomposites; (viii) Optimize morphology and composition to tailor optical absorption for solar radiation and maximize electrical output; and (ix) Prepare and evaluate performance of complete photovoltaic device structure.

Technical Activities Performed (Progress)

A 900 sqft. wet lab space was equipped to allow the synthesis, processing, and characterization of nanophase materials such as inorganics, organics, metals, and composites of these materials. Specifically, two vacuum deposition chamber for the synthesis of nanophase materials were set up. One chamber uses a four-pocket effusive evaporation cell and the second chamber uses a CO₂ laser to evaporate materials. Wet-chemical processing, pressing of green bodies, and sintering in an air-furnace can be performed. A Nd:YAG/OPO laser system with a mono-chromator and CCD arrays for the visible and infrared wavelength range, as well as a cryo-cooler allow for optical characterization such as fluorescence and excitation measurements at sample temperatures between 8°K and 475°K.

1. Transparent Ceramics for Infrared Window and Laser Applications

a. Infrared Window Applications

Without any further processing, the nanophase yttria powder was dry-pressed in a stainless steel die under 632 MPa for 30 minutes, resulting in a 12.7 mm diameter and about 2 mm thick green body. The green body was subsequently sintered at 1600°C for 2 hours in air in a Lindberg/Blue box furnace, resulting in a translucent ceramic with a relative density of about 99.4%. Density measurements were performed using the Archimedes principle, and a theoretical density of 5.01 g/cm³ was used for the calculation of the relative densities. Subsequently, the ceramic was HIPped at 1650°C in an Ar pressure of 203 MPa for 6 hours.

Figure 1(a) shows an image of the yttria ceramic after lapping and polishing. The unpolished ceramic was about 11 mm in diameter, 1.5 mm thick, and translucent enough to distinguish letters. After lapping and polishing the thickness decreased to about 0.5 mm. The sample flatness was tested with $\lambda/20$ optical flats and showed flatness within 1 - 3 fringes, with only slight rounding near the outer edge of each face. Letters are clearly visible and can be read through the ceramic.

Figure 1(b) shows the transmission of the 0.5 mm thick polished ceramic yttria sample. Yttria has a theoretical transmission of just over 80% over the visible and infrared wavelength range. Transmission spectra of single-crystal yttria and polycrystalline yttria can be found elsewhere.¹ Optical scattering, particularly in the visible wavelength range, limits the transparency of most ceramics.^{7,8}

Figure 1(c) shows an SEM image of a transparent ceramic after it was etched to expose grain boundaries. Linear intercept and multiplication with a factor of 1.56 yielded an average grain size of $21.5 \pm 11.1 \mu\text{m}$.^{9,10} Large pores are visible, further indicating that the less than ideal transparency is due to optical scattering.

⁷ N. Saito, S. Matsuda, and T. Ikegami, "Fabrication of Transparent Yttria Ceramics at Low Temperature Using Carbonate Derived Powder," J. Am. Ceram. Soc. 81 [8] 2023-8 (1998)

⁸ L. Wen, X. Sun, Q. Lu, G. Xu, and X. Hu, "Synthesis of yttria nanopowders for transparent yttria ceramics," Opt. Mater. doi:10.1016/j.optmat.2005.09.003

⁹ P.-L. Chen and I.-W. Chen, "Sintering of Fine Oxide Powders: I, Microstructural Evolution," J. Am. Ceram. Soc. 79 [12] 3129-41 (1996)

¹⁰ J. S. Reed "Principles of Ceramic Processing," 2nd edition, Wiley-Intersciences, New York 1995

Knoop hardness and Vickers hardness measurements were performed on the polished and etched sample. Measurements showed hardnesses of 792HK₁₀₀, 704HK₅₀₀, and 767HV₁₀₀, in good agreement with published data.¹

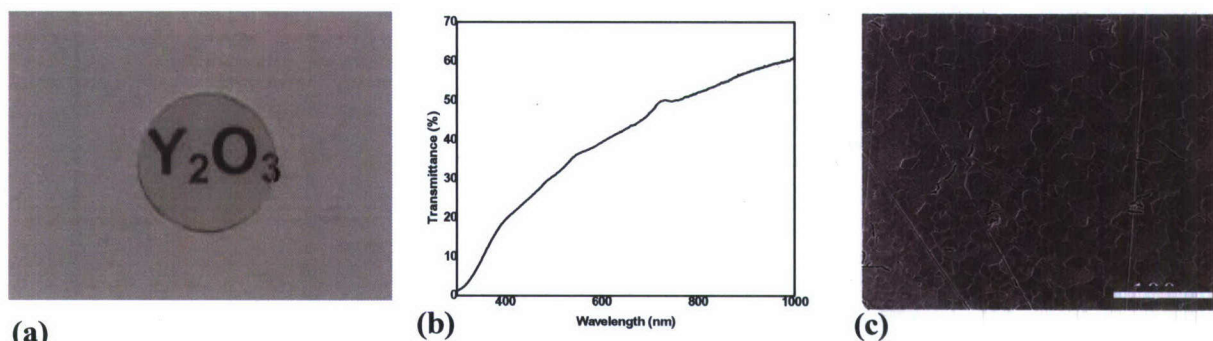


Figure 1. Image of yttria ceramic after it was lapped and polished (a). Transmission of polished ceramic yttria sample (b). SEM image of transparent yttria sample. The straight lines were caused by the polishing process (c.)

b. Laser Applications

Nanophase Er,Yb:Y₂O₃ is routinely synthesized in our lab. Figure 2 shows x-ray diffraction data of the as-prepared and annealed powder and Figure 3 shows the near-infrared luminescence of the annealed powder. The powder has been pressed into pellets (6 mm diameter and 1-2 mm thick) and sintered. Two-stage sintering in air and in vacuum and single-stage vacuum sintering have been used to consolidate the material. Vacuum sintering and two-stage sintering in vacuum have led to micron-sized grains. Two-stage sintering in air has kept the grain size below 150 nm. Our first experiments using two-stage sintering led to ceramics with about 65% theoretical density. Through improved temperature and time schedules we have been able to increase the density to 92%. Further improvements are expected through refinement of the sintering schedules and the use of hot isostatic pressing (HIP).

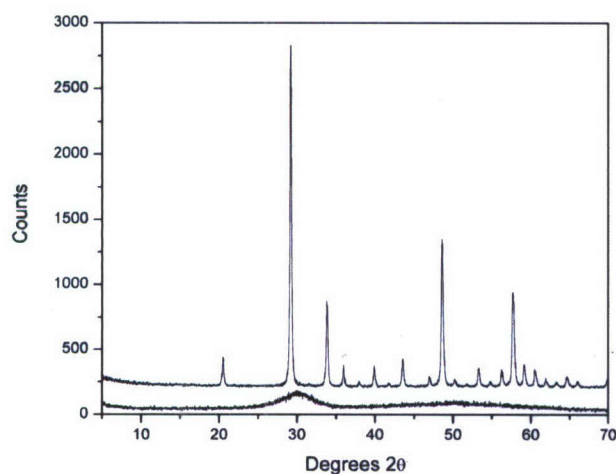


Figure 2. Powder XRD scans of as-prepared Er,Yb:Y₂O₃ nano-particles (bottom) and annealed Er,Yb:Y₂O₃ nano-particles (top, offset by 200 counts).

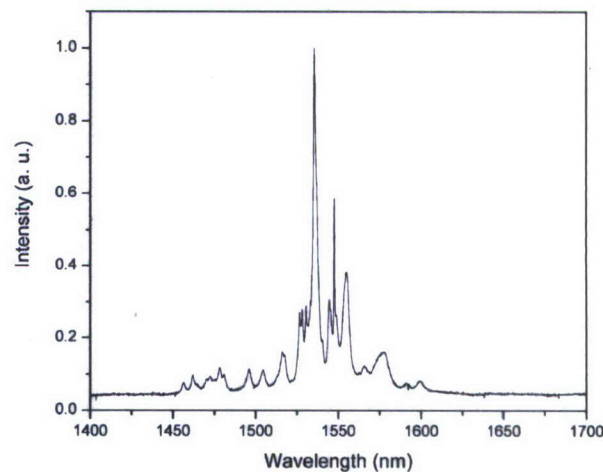


Figure 3. Near-infrared luminescence of annealed Er,Yb:Y₂O₃ nanoparticles.

Optical characterization of the ceramics has confirmed the absorption of 940 nm and 973 nm light by the Yb ions with subsequent energy transfer to the Er ions, and the resulting near-infrared luminescence in the eye-safe wavelengths range, as well as upconversion luminescence at green and red visible wavelengths.

2. Broadband-Absorbing Polymer-Metal Nanocomposites for Photovoltaic Applications

Polymer-metal nanocomposites (Teflon AF / Ag and PMMA / Ag) with various metal concentrations have been prepared and their optical properties characterized. Figure 4 shows SEM images of Teflon AF / Ag nanocomposites with two different metal concentrations and their corresponding absorption profiles. Adjusting the polymer-to-metal ratio allows one to tailor the optical absorption of the nanocomposites for specific applications, such as photovoltaic (left) and broadband-absorbing sensor (right).

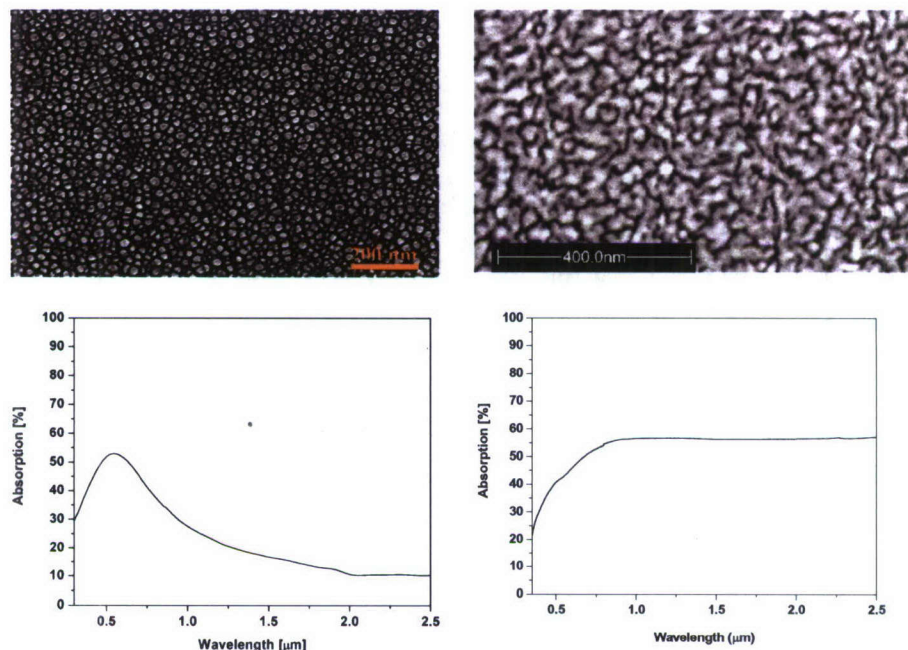


Figure 4. SEM images of Teflon AF / Ag nanocomposites with different metal concentrations and their corresponding absorption profiles

Figure 5 highlights the overlap of the solar radiation spectrum with the absorption of a polymer-metal nanocomposite. For comparison purposes, the responsivity curve for silicon (used for standard solar cell technology) is also shown.

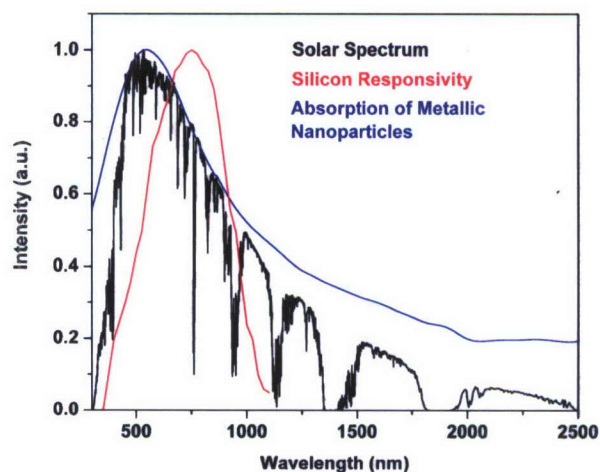


Figure 5. Solar radiation spectrum compared with the absorption of a polymer-metal nanocomposite and silicon responsivity.

Results & Discussion

Transparent yttria ceramics were successfully prepared from commercially available nanopowders. Further refinement of the processing steps is expected to result in ceramics with even smaller grain size and reduced scattering in the visible wavelength region. Erbium and ytterbium codoped yttria nanoparticles were successfully synthesized and characterized. Initial sintering resulted in ceramics with 92% theoretical density. Further optimization using results for the undoped yttria ceramics is expected to lead to transparent Er,Yb:Y₂O₃ ceramics.

Polymer-metal nanocomposites with varying metal content have been prepared. It was shown that the optical absorption profiles of these composites can be tailored to match the solar radiation. Further experiments are needed to characterize the electrical properties of these composites.

Part II

Alternative energy storage using first-principles modeling and simulations

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Abstract

The first-principles modeling and simulations effort concentrated on the fundamental reaction mechanism of hydrogen storage reactions in solids. We are currently working towards addressing fundamental roadblocks in nearly ambient regeneration pathways for AlH_3 , a complex metal hydride, and borohydrides. We use first-principles theory to explore new reaction pathways, investigate the role of catalytic additives, and work with experimental collaborators to follow up on promising theoretical predictions. Most of these phenomena have their roots in the electronic structure of solid surfaces where the regeneration reaction with molecular H_2 starts. We used first-principles theories to screen such events and provided surface vibrational spectroscopic signatures for identifying the mass transport species during the regeneration process. Any progress towards a high-density, high-purity and reversible hydrogen storage source will also aid the long-term prospect of fuel cells in many areas of stationary and mobile use, including defense related applications.

Background

Alane clusters (AlH_x) are believed to be the ubiquitous intermediates in hydrogen storage reactions in a series of aluminum hydrides (such as AlH_3 , LiAlH_4 , NaAlH_4 etc.) currently considered for hydrogen storage. A direct regeneration of all these materials will require chemisorption of H_2 on Al, a process with a very high activation barrier (>1 eV) for most common surface terminations of Al. We have demonstrated in recent studies that catalytically active Ti centers on a Ti-doped Al surface lowers this barrier and acts as a pump that generates transient hydrides forming alane species. We that the presence of alanes on a doped Al surface can explain the regeneration reaction of sodium alanate. In this case, the presence of NaH grains in the depleted material acts as a chemical sink for the alanes and regenerates NaAlH_4 (and Na_3AlH_6 , another intermediate) under ambient conditions. As further evidence for the formation of alanes, we recently managed to trap these incipient alanes from Ti-doped Al particles in THF-suspended solutions at room temperatures and 35atm H_2 pressures. The alanes formed on the surface precipitated as a solid consisting of 1:1 adduct between AlH_3 and triethylenediamine (TEDA). This AlH_3 -TEDA polymeric forms only in the presence of dilute amounts of Ti in the Al particles. We do not have any evidence that suggests the alanes are formed in a high enough concentration to form a bulk AlH_3 phase. The research performed in 2007 has provided a critical understanding about alanes allowing us to lower H_2 pressure required for regeneration. We have started to build a similar case for boranes (B_xH_y) which are the analogs of alanes in borohydride chemistry, which need to form at a higher rate for faster regeneration of borohydrides.

Objectives

The overall objective provides a pathway for convenient regeneration of hydrogen storage materials for fuel-cell and automobile applications. In this effort, we used a high-performance computing infrastructure to perform large scale *ab initio* calculations, first-principles and classical molecular dynamics (MD) simulations. The theoretical calculations are performed in close collaboration with experimental

researchers. By sharing the ideas generated using first-principles calculations we can try to maximize the impact of our predictive capabilities.

Technical Approach by Task

The following tasks constitute the core of our technical approach:

- A range of theoretical techniques were used for the calculation of surface catalytic pathways for H_2 chemisorption. For surface calculations, we used Kohn-Sham density functional theory (DFT) under generalized gradient approximation (GGA) with well-tested ultrasoft plane wave pseudopotential basis sets. This technique is also supported by quantum chemical theories for cluster calculations of electronic structure and spectroscopic details of chemically important species studied on the metal surfaces.
- DFT-MD simulations of the dynamics of alane clusters have been performed to follow chemical dynamics. To obtain information on the diffusion of alanes and interconversions between different bulk phases, we used both Born-Openheimer MD (BOMD) and Car-Parrinello MD (CPMD) simulations.
- We performed partial Hessian based, all-electron DFT calculations of surface vibrational spectra and helped to identify different Al-H vibrational models with *in situ* surface IR absorption spectra of the corresponding reactions. The mechanisms we uncovered constitute a unique insight into the chemistry and promise to be a major achievement in this field.
- We also calculated binding energies of the alane and borane clusters. These, in combination with IR spectrum, are used to follow temperature dependent H_2 desorption (TPD spectrum with IR probe) and uncovered H_2 desorption mechanisms from the Al surface.

Technical Activities/Progress

- (a) **Hydride-borohydride, borohydride-imides and other mixed materials as probable hydrogen storage material:** $LiBH_4$ - MgH_2 has effective hydrogen storage capacity of 9 wt.%. The rehydrogenation temperature is too high for practical applicability of these materials. The search for a catalytic route to lower the rehydrogenation temperature is challenging due to the lack of fundamental understanding of the processes behind the hydrogen storage reaction. Researchers at HRL laboratories, LLC, CA and Brookhaven National Laboratory are actively working with these materials. There is also interest in similar materials in the Materials and Process Laboratory, GM Research and Development center where borohydride-imides ($LiNH_2$ - $LiBH_4$) are being studied as a future hydrogen storage material. The aim of our research to provide theoretical models for the regeneration of the fuels. Our results continue to improve understanding of the catalytic processes that can remove the technological bottlenecks. In 2007, we came up with a new composition and catalytic pathway that we plan to synthesize in 2008. We submitted a summary of our results to *Journal of Physical Chemistry C* that is currently under review.
- (b) **Metastable metal hydrides: entropy guided screening of hydrogen storage materials:** The proposed research explores a new area of hydrogen fuels broadly classified as metastable metal hydrides (MMHs). Unlike the stable metal and chemical hydrides now receiving study, MMHs have low enthalpy of formation, which reduces the heat input required to release hydrogen and promotes more rapid decomposition kinetics at low temperatures. AlH_3 in particular also meets the DOE volumetric and gravimetric storage goals; thus, it could be an ideal hydrogen fuel. This research is currently pursued in collaboration with our partners in Brookhaven National Lab who are part of DOE's Metal Hydride Center of Excellence (MHCoe). In 2007, we made a new polymeric solid AlH_3 -triethylene diamine as a hybrid material, which holds hydrogen and can be regenerated under 35 atm pressure. These results appeared in *Journal of Physical Chemistry C* in 2007.

- (c) **Surface IR study of hydrogen chemisorption and mass transport in solids:** This is an ongoing study to identify the role of chemical reaction intermediates during the hydrogen storage reaction in metal hydrides and complex metal hydrides. This research started as part of a theory guided experimental investigation funded by DOE's Hydrogen Fuel Initiative. The research has now advanced to using surface IR and first-principles modeling of surface vibrational modes for understanding molecular intermediated Al-based hydrides, called alanes. We recently uncovered these clusters and their roles as a mass-transport intermediate. This work is now continuing in active collaboration with the surface spectroscopy group of Professor Yves Chabal at the University of Texas in Dallas. We submitted our results to the *Journal of American Chemical Society* for peer review and it has recently been accepted subject to a few changes that are being submitted.

Results and Discussion

Currently, the 2010 system gravimetric target established by DOE is 6 wt% H₂ and 3 minutes for the regeneration of the storage tank in automobile applications. Unfortunately, most of the existing systems are probably not going to achieve all the targets without a significant breakthrough. Our approach uses the fundamental atomistic understanding to search for solutions. In 2007, we have been successful in demonstrating the promise and made significant progress towards the target and performance goals. Our results have been presented by our collaborators in different conferences including an APS meeting, AVS meeting, and DOE annual merit review in 2007.

Part III

Charge Transport in Solid Oxide Fuel Cells and Organic Light Emitting Diodes

Gregory Exarhos, Principal Investigator
Pacific Northwest National Laboratory

A. Charge Transport in Solid Oxide Fuel Cells (SOFC)

Task A addressed the dissociative adsorption of oxygen at an oxide electrode followed by subsequent ion transport through the electrode and the underlying oxide electrolyte. Three key elements comprised the research under this task. The first element involved furthering our understanding of the Triple-Phase-Boundary that is associated with the electrochemically-driven ion transport process. This boundary includes the gas phase (oxygen), the electrode (electron transport medium), and the electrolyte (ion transport medium). In this research area, the goal was to investigate how the interfacial architecture may be designed to promote charge transport. To that end, colloidal self-assembly approaches were used to fabricate textured interfaces as a means to increase the surface area of the TPB region. Results from our BES-supported nanoscience project were leveraged and guided the construction of these interfaces. Prior to the end of the program, we had successfully produced a textured interface and we intended to structurally characterize it and evaluate the effect of this tailored interface on interfacial transport. Results were intended to illustrate the efficacy of designed interfacial architectures on charge transport and were intended for publication in the Journal of Physical Chemistry and the Journal of the Electrochemical Society. *(Project terminated before enough data was generated to write the paper. Other funding sources are being explored to complete this work.)*

The second element in Task A involved development and substitution of a new electrode material for the currently used oxide perovskite. Chief goals were to engineer an electrode that would promote dissociative adsorption of oxygen, and also that would support relatively high ion currents at temperatures significantly lower than 750 C required by existing materials. A spinel material originally studied in another of our BES projects may be a strong candidate electrode. Initial measurements on the polaron conductor (nickel cobalt spinel oxide) indicated that this material can support high current flows in oxygen environments at a few hundred degrees Celsius. These measurements on sputtered films were encouraging but needed to be repeated on electrode films of varying thickness and porosity. Had we been successful at demonstrating enhanced current flow through this material, a subsequent patent and research papers (perhaps in Thin Solid Films) would have resulted. *(Paper submitted to journal and accepted for publication.)*

The third element in Task A involved setting up a high temperature Raman microprobe spectroscopy experiment to follow, in real time, chemical changes at the tailored interface under conditions of current flow in an oxygen environment. A cell was constructed and interfaced to the Raman spectrometer. Initial measurements were on a cerium dioxide solid electrolyte to identify the equilibrium defect states that accompany oxygen ion diffusion. This work was to be published in the Journal of Physical Chemistry. *(Project terminated before enough data was generated to write the paper.)*

B. Charge Transport in Organic Light Emitting Diodes (OLED)

Task B involved studies of charge transport across soft interfaces that are prevalent in OLED's. Work here proposed to develop new materials to promote charge migration and reduce non-radiative losses.

This task included computer-modeling studies designed to simulate light emission dynamics as a function of the molecular geometry of the emitting metal ion complex. We have found that steric hindrance induced by asymmetric ligands incorporated in the complex can affect light emission (both wavelength and intensity). The aluminum quinolate complex is used by everyone to study emission processes and build devices. However, the nature of the complex and in particular its isomeric purity remain hotbeds of contention within the scientific community. Staff here has pursued this question through careful synthesis and magnetic resonance characterization of the material. In addition, a new model quinolate material (the zinc tetramer) has been discovered. This material has been prepared isomerically pure and helped us understand electroluminescent properties of the model complex. Work has been presented at the Spring MRS meeting and was to be presented at the Fall MRS meeting in Boston with appropriate reference to ONR funding through WSU. *(Two papers have been published.)*

Within Task B, work also had focused on understanding hole transport from the currently used n-type TCO electrode into an organic layer. We developed a p-type polaron conductor material that shows promise as an efficient electrode for hole injection. Plans before the program ended were to better characterize this material (eg. Work function determination) and incorporate it in a device. Scoping experiments have been promising. *(Project terminated before enough data was generated to write the paper.)*

Specific Research Activities Pursuant to this Project

Both Tasks:

Conduct literature search (technical literature, patent literature), obtain relevant papers either electronically or by ordering through the library; read collected papers and discuss papers with colleagues; based upon these papers, revise research agenda so as not to duplicate already published work; these literature searches are conducted regularly (at least weekly) to be cognizant of recent advances in these rapidly evolving fields.

Design and implement experiments in accordance with original research proposal submitted to WSU.

Task A Activities included the following:

1. Task A – synthesis of tailored ceramic interface based upon published colloidal templating routes and modified for this task.
2. Task A – verification of electrode microstructure by imaging studies
3. Task A – RF sputter deposition and solution deposition of spinel electrode layers (requires synthesis of 2 inch diameter sputtering target – prepared at PNNL – determining sputter deposition conditions to deposit conducting layers – characterizing the material – XRD, IR – determining solution spin casting parameters, solution deposition of films and subsequent characterization. Insure proper handling of chemical wastes.
4. Task A – Measurement of conductivity in these layers at difference ambient temperatures
5. Task A – Design of Raman backscattering experiment to follow in real time oxygen adsorption phenomena at electrode surfaces – Raman measurement leverages previous IR data on this system showing oxygen ion defect formation at different temperatures and ambient oxygen environments; interfacing of heated sample stage to Raman microprobe spectrometer; provision for so-measurements of sample conductivity also incorporated into the stage.
6. Task A – Raman measurements of ceria-based electrolytes to understand resident defect structure and how that structure changes at different temperatures and ambient oxygen concentrations
7. Task A – Data collection (detailed in laboratory notebooks) and analysis of data
8. Task A – Discussion of results and drafting of papers for publication in peer-reviewed technical Journals

Task B activities included the following:

1. Task B – Electronic structure modeling – parameterize computer codes for determining equilibrium geometries of selected metal-ligand complexes; testing the effect of ligand asymmetry on equilibrium geometry; modeling electronic structure of selected geometries; calculating dynamic optical emission spectra of selected complexes – parallelizing computer codes to run on evolving computer cluster to facilitate calculations (we have implemented our own cluster to do these calculations rather than paying to use other computing facilities) procurement of disk read/write and storage capability to enable these calculations.
2. Task B – Based upon computer modeling studies, provide direction to synthesis part of the project-synthesize metal ligand clusters – procure chemical and glassware to perform synthesis – all work done in controlled environment (no oxygen or water vapor) – purify metal ligand clusters and verify composition and structure – GC/MS, MNR, IR, Raman – clean up waste chemicals and insure proper handling of chemical wastes – determine conditions for vapor deposition of thin films of metal complexes onto different substrates
3. Construct OLED device from newly synthesized materials and test device properties including energy input to light output – test the efficacy of new p-type electrode as a hole injector for an OLED device

Publications

1. H. Eilers "Synthesis and characterization of Nanophase Yttria co-doped with Erbium and Ytterbium," *Mater. Lett.* 60 (2), 214 (2006)
2. A. Biswas, H. Eilers, F. Hidden, O. C. Aktas "Large broadband visible to infrared plasmonic absorption from Ag nanoparticles embedded in a Teflon AF matrix," *Appl. Phys. Lett.* 88, 013103 (2006)
3. H. Eilers, A. Biswas, T. D. Pounds, M. Grant Norton, and M. ElBahri, "Teflon AF/Ag nanocomposites with tailored optical properties," *J. Mater. Res.* 21, 2168 (2006)
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Books and Chapters

1. H. Eilers "Synthesis and consolidation of nanophase Yttria (Y_2O_3)," in *Windows and Dome Technologies and Materials IX*, edited by Randal W. Tustison, *Proceedings of SPIE Vol. 5786* (SPIE, Bellingham, WA, 2005) pp. 234 – 241
2. H. Eilers "Eye-safe Er,Yb: Y_2O_3 ceramic laser materials," in *Windows and Dome Technologies and Materials IX*, edited by Randal W. Tustison, *Proceedings of SPIE Vol. 5786* (SPIE, Bellingham, WA, 2005) pp. 242 – 250

Presentations

1. H. Eilers "Synthesis and consolidation of nanophase Yttria (Y_2O_3)," in *SPIE Defense & Security Symposium, Windows and Dome Technologies and Materials*, Orlando, FL 2005
2. H. Eilers "Eye-safe Er,Yb: Y_2O_3 ceramic laser materials," in *SPIE Defense & Security Symposium, Windows and Dome Technologies and Materials*, Orlando, FL 2005

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14. ABSTRACT The scientific activities carried out in this project focused on characterization and development of advanced materials. These activities were divided into three parts. Part I focused on nanophase enhanced optical devices: development of transparent ceramics for infrared window and laser applications, and development of nanocomposites for photovoltaic applications. Part II focused on alternative energy storage using first-principles modeling and simulations. The research in Parts I and II was carried out at Washington State University. Part III focused on charge transport in solid oxide fuel cells (SOFC) and organic light emitting diodes (OLED). The research in Part III was carried out, under a subcontract, at the Pacific Northwest National Laboratory (PNNL). Because of the distinct nature of the three projects in this grant, the text of this final report consists of the activities for each of these three projects.					
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